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Insight from ZIF-4

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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

Disorder-Order Transition in Melt-Quenched MOF Glass: Insight from ZIF-4

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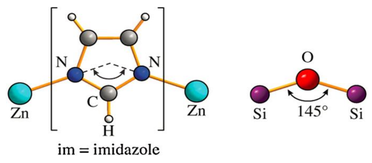
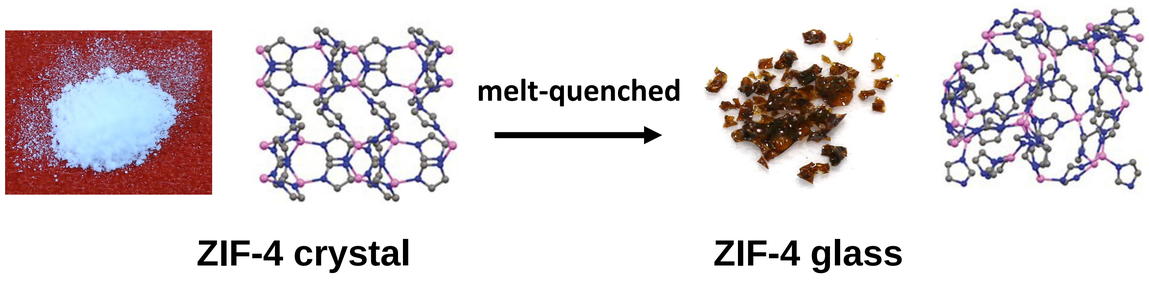
Introduction

- Metal-organic frameworks (MOFs) are a new family of glass-formers that adopt networked structures of metal ions connected by organic ligands via coordination bond[1-3].
- Zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs that possess high chemical and thermal stability, have attracted increasing attention..



Similarity in structural bonding units between ZIF-4 and SiO_2.

- The majority of MOFs decompose directly upon heating, instead of melting. But a few of MOFs can be vitrified, e.g., ZIF-4, if it can be melted before decomposed[1].

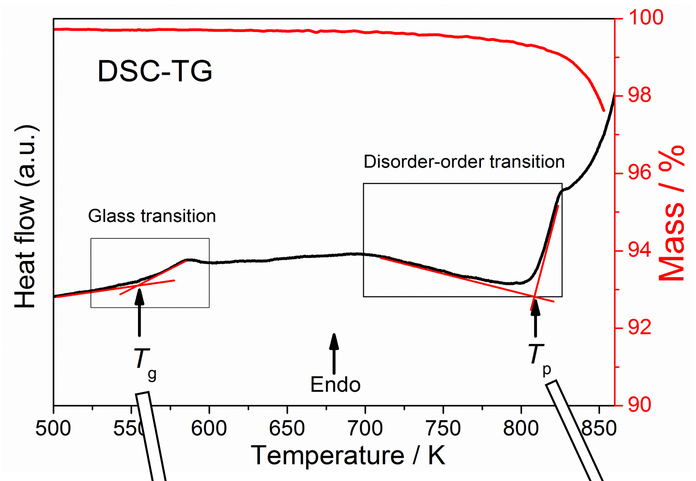


ZIF-4 crystal **ZIF-4 glass**

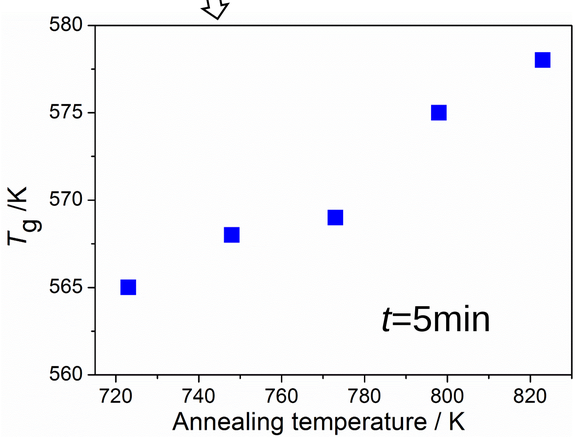
- Does ZIF-4 glass recrystallize like most of inorganic glasses?
- How do the structure or topology vary in ZIF-4 glass upon heat-treatment above T_g?

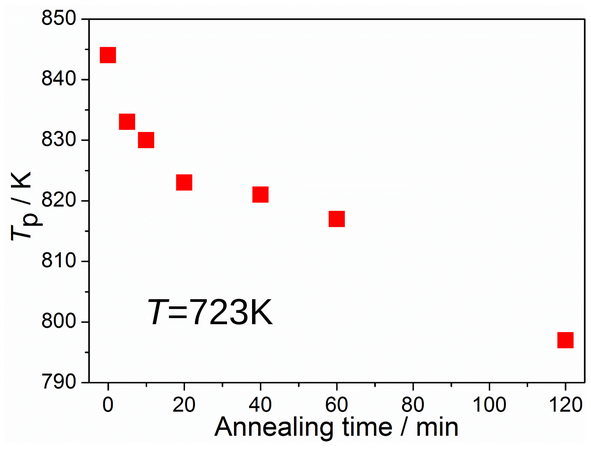
1. T. D. Bennett, J.-C. Tan, Y. Z. Yue, et al., Nat. Commun., 6, 8079 (2015).
2. T. D. Bennett, Y. Z. Yue, P. Li, et al., J. Am. Chem. Soc., 138, 3484 (2016).
3. H. Tao, T. D. Bennett and Y. Z. Yue, Adv. Mater., 1601705 (2017)

Thermal response of ZIF-4 glass



- A distinct exothermic peak appears around T_p prior to decomposition (see mass drop).
- How does the structure of ZIF-4 glass change during exothermic response?
- At which length scale do the "crystals" form?

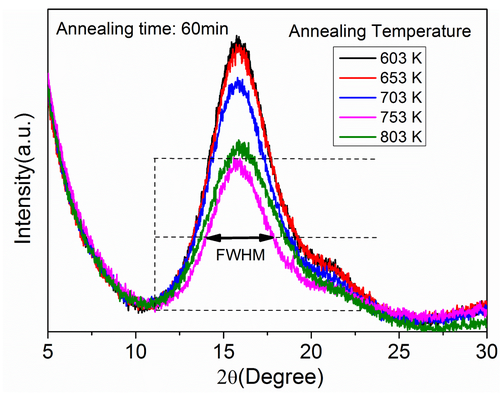


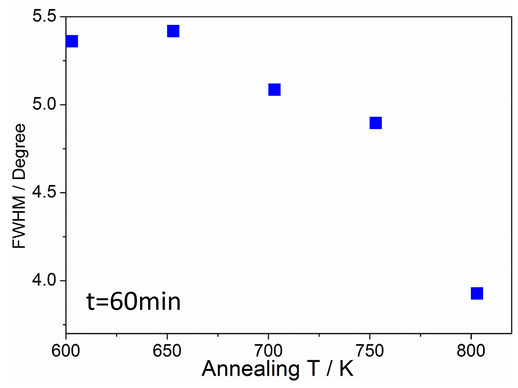


- T_g increases with annealing temperature, indicating the enhanced connectivity of the network in heat-treated ZIF-4 glass.
- T_p decreases with annealing time, indicating the ordered domains occur, which make nucleation easier.

Disorder-order transition in ZIF-4 glass

Powder XRD



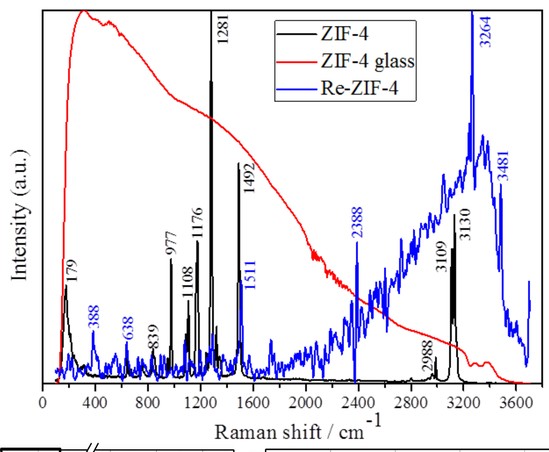


No Bragg peaks occur, hence there is no long-range order, but nano-ordered domains might appear.

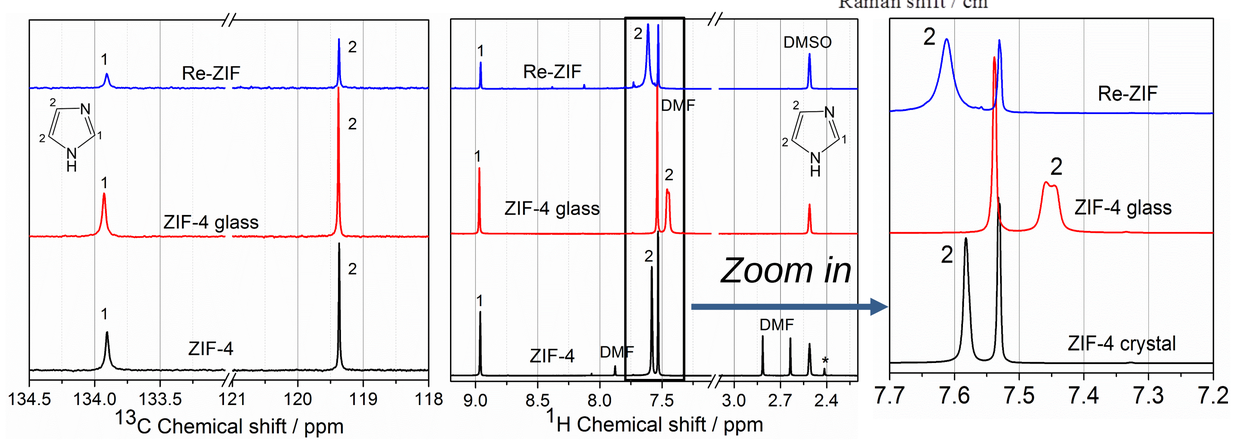
- The FWHM decrease with annealing temperature.
- This implies an increase of the degree of order and the ordered domain size.

Raman

- There are no peaks for ZIF-4 glass.
- Raman peaks occur for the heat-treated ZIF-4 glass.
- These confirm that the crystals appear at nano-scale, which are larger than medium-range order structure.



Liquid-state NMR



- Local environment around the ^{13}C is almost the same.
- ^{1}H resonances of crystal, glass and "recrystallized" sample appear at different chemical shifts.
- These indicate that heat-treatment causes the structural change.

Conclusion

- Disorder-order transition in ZIF-4 glass is discovered.
- After heat treatment, some ordered domains are formed. However, ZIF-4 glass is still in amorphous state.
- The mechanism of this disorder-order transition remains elusive.
- New techniques should be applied to characterize structural features during the transition, such as neutron scattering.

Why neutron scattering?

Disorder-order transition in ZIF-4 glass has been studied by performing heat-treatments and structural analyses. Neutron techniques are expected to help to answer these questions :

- At which length scale the order-disorder transition occur in ZIF-4 glass?
- Does the heat treatment induce change of coordination bonds (Zn-N) in terms of bonding length and angle, and recovery of the distorted network?